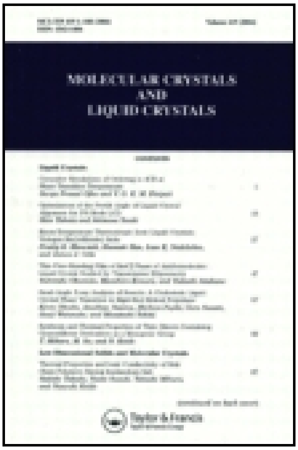

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Spectral Effects in Cholesteryl Myristate for the Region of Liquid Crystal Phase Transitions

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For the first time we report on temperature dependence of Davydov splitting value FTIR spectra study for the in-phase CH_2 rocking vibrations of methylene chains in crystalline cholesteryl myristate ($CholC_{14}$) for the temperature region from 100 K to the isotropic liquid transition point.

A statistic dynamic model in terms of stochastic equations is used to explain the obtained results by accounting the damping of vibrational excitons on positional defects. Genesis of such defects is related with transition in different liquid crystal phases (smectic phase and cholesteric phase for cholesteryl myristate). Good agreement between the experimental data and the results of such dependence computer fitting is observed.

Keywords: cholesteric; Davydov splitting; IR spectra; liquid crystals; positional defect; smectic

INTRODUCTION

It is known [1–3] that in long-chain crystals in the different temperature range the molecules can perform the disordered motions of different types. It is clear that any distortions in the periodic location of atoms in the plane perpendicular to the long axis of the molecules should result in some peculiarities of intermolecular interactions. In particular, one could expect changes in the resonance dynamic intermolecular interaction (Davydov splitting of vibrational excitons) in the different disordered phases.

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Earlier, when studying the effects of the intermolecular interaction and the problems of molecular dynamics in crystals of homologous series of normal paraffins, α-olefins, n-carboxylic acids, cholesteryl n-alkanoates and aromatic compounds by the method of infrared spectroscopy, in particular, the temperature dependence of spectral peak positions for Davydov components of the intramolecular vibrations was observed [1–6]. These spectral components approach each other in the region of the order – orientational disorder phase transition. For nowadays, there is no commonly accepted explanation of the observed temperature dependence.

In this work we report on temperature dependence of Davydov splitting value FTIR spectra study for the in-phase CH_2 rocking vibrations of methylene chains in crystal cholesteryl myristate ($CholC_{14}$) for the temperature region from 100 K to the isotropic liquid transition point. In this region take place such phase transitions: single crystal (SC) – smectic (Sm), smectic – cholesteric (Chol), cholesteric – isotropic liquid (IL) [4].

Also we use mechanisms, which adequately describe the observed effects of temperature dependence for cholesteryl myristate as example. These mechanisms are related with the damping of vibrational excitons in liquid crystal mesophases due to interaction of these excitons with positional defects. Genesis of such positional defects is related with transition in different liquid crystal phases of compound.

RESONANCE DYNAMICAL INTERMOLECULAR INTERACTION IN MOLECULAR LIQUID CRYSTALS (THEORY)

Low-Temperature (Order) Phase of Crystal

In general, the eigenfrequencies for transversal vibrations, which correspond to the components of Davydov multiplets can be found with the use of the standard procedure, which involves the diagonalization of the matrix [7]

$$\{\hat{\omega}_0^2 - \hat{D}\}, \tag{1}$$

when passing to the coordnates of symmetry, which are transformed according to irreducible representations of corresponding factor-group. Here $\hat{\omega}_0^2$ is a diagonal (in the coordinates of symmetry) matrix of squares of frequencies for intramolecular vibrations in the crystal in the absence of the resonance dynamic intermolecular interaction; $\hat{D}$ is the corresponding matrix of the resonance dynamic intermolecular interaction.

For a crystal with two molecules per unit cell, one can present the frequencies of Davydov multiplets components for j-th normal fundamental vibrational mode $\omega^{(j)}$ (wave vector $k = 0$) in the convenient form [8].

$$\begin{aligned} \omega_1^{(j)} &\approx \omega_0^{(j)} + \Delta\omega^{(j)}, \\ \omega_2^{(j)} &\approx \omega_0^{(j)} - \Delta\omega^{(j)}. \end{aligned} \tag{2}$$

Here $\omega_0^{(j)}$ is the frequency of j-th intramolecular vibrations, not perturbed by the resonance dynamic intermolecular interaction;

$$\Delta\omega^{(j)} \approx \frac{\widehat{D}}{2\omega_0}$$

is a frequency shift, caused by the resonance dynamic intermolecular interaction. The expression (2) is written, when neglecting the values of second order of smallness.

And, at some approximations, the vibrational Davydov splitting value, $\Delta\omega$, from (2) is defined as

$$\Delta\omega = \omega_1^{(j)} - \omega_2^{(j)} = \frac{D_{(l,n)}^{(j)}}{\omega_0^{(j)}}. \tag{3}$$

Liquid Crystal Phase

Here we describe the contribution of the intermolecular interaction effects and molecular dynamics for liquid crystal on the formation of the spectral bands of intramolecular vibrations in the framework of stochastic equations [9–11].

For this purpose we consider $(N + 1)$ reactively coupled identical oscillators, which form an actual system (cluster) with $(N + 1)$ states of the selected optical (IR) active mode in the bath from positional disordered molecules. At some approximations, the time correlation function of this selected mode is described by the equation

$$\frac{d}{dt}\widehat{G}(t) = \widehat{G}(t)\left[i\widehat{\omega} + \widehat{\Gamma} + \gamma\widehat{1}\right], \widehat{G}(0) = 1 \tag{4}$$

The time correlation function $\widehat{G}(t)$ includes:

1) oscillations ($\widehat{\Omega}$ is the matrix of oscillations);
2) reactive relaxation due to the interaction between the oscillators of the actual system ($\widehat{\Gamma}$ is a matrix of reactive relaxation);

3) pure relaxation γ due to the anharmonic interaction of the selected vibrational mode with vibrations of the bath and due to the reorientation of molecules.

The corresponding normalized spectral function $\overset{\frown}{J}(\omega)$ can be determined from $\overset{\frown}{G}(t)$ with the use of Fourier transformation:

$$\overset{\frown}{J}(\omega) = \frac{1}{\pi}\int_{0}^{\infty} \overset{\frown}{G}(t)e^{-i\omega t}dt. \tag{5}$$

To determine the matrix of frequency oscillations $\overset{\frown}{\Omega}$, which is a part of the expression (4), we write the stochastic Hamiltonian of the system in the form

$$\overset{\frown}{H}(t) = \overset{\frown}{H}^{(0)}(t) + V^{(1)}(t). \tag{6}$$

Here $\overset{\frown}{H}^{(0)}(t) = \overset{\frown}{P}(t) + V^{(0)}(t)$ is the Hamiltonian of the system, which describes a weak influence of the thermostat; $V^{(0)}(\mathbf{t})$ is the stochastic potential energy of interactions between the molecules of the actual system and the bath; $V^{(1)}(t)$ is the stochastic potential energy of interactions between the molecules of the actual system. For convenience we assume that it is precisely the resonance dynamic intermolecular interaction gives the main contribution to the perturbation of frequencies, which are elements of the oscillations matrix, $\overset{\frown}{\Omega}$, and determines the magnitudes and the structure (symmetry) of the actual system.

Then, taking into account the processes of the discrete frequency modulation, we write the elements of the oscillations matrix, $\overset{\frown}{\Omega}$, for i-th component of Davydov multiplet of j-th normal vibration in the form

$$\left(\Omega_i^{(j)}\right) = \delta_{l,n}\left(\omega_0^{(j)} + n\Delta\omega_i^{(j)}\right), \quad l, n = 0, 1, 2, \ldots, N. \tag{7}$$

The elements of the reactive relaxation matrix $\overset{\frown}{\Gamma}$ which are determined by the rate of molecules transition to their excited (positional disordered) states can be written in the following form:

$$(\Gamma)_{l,n} = R\left[(N-n)\delta_{l+1,n} + kn\delta_{l-1,n} - (N - n + kn)\delta_{l,n}\right] \tag{8}$$

Here the frequency modulation of the intramolecular vibrational mode due to the resonance dynamic intermolecular interaction is switched on with the rate R and switched off with the rate kR. These rates can be presented in the form of the adapted Arrhenius law:

$$R = \sum_{m=1}^{p} A_m \exp\left(-\frac{E_{Am}}{k_B T}\right), \quad k = \sum_{m=1}^{p} \exp\left(\frac{\Delta S_m T - \Delta E_{Am}}{k_B T}\right), \tag{9}$$

where E_{Am} is the activation energy; k_B is Boltzmann constant; T is absolute temperature; ΔS_m, ΔE_{Am} are, respectively, variations of entropy and activation energy, required for the turning out the discrete modulation processes in the excited state m; p is the number of excited states (or number of liquid crystal mesophases).

Having taken into account the binomial distribution of states for the actual system and having performed the averaging over the ensemble, we obtain the corresponding spectral function

$$\widehat{J}(\omega) = \frac{1}{\pi}\left\langle \left[i\left(\omega - \left\langle \Omega_i^{(j)} \right\rangle\right) - \gamma - \Gamma \right]^{-1} \right\rangle, \tag{10}$$

where $\langle \ldots \rangle$ denotes averaging. Then the average value of the vibrations frequency for the i-th component of Davydov multiplet of j-th normal vibration is determined as follows

$$\left\langle \Omega_i^{(j)} \right\rangle = \omega_0^{(j)} + \Delta\omega_i^{(j)} \frac{N}{1 + \sum\limits_{m=1}^{p} \exp\left(\frac{\Delta S_m T - \Delta E_{Am}}{k_B T}\right)} \tag{11}$$

The analysis of the expressions (11) shows that, when the temperature increases, the values of Davydov components frequencies, $\langle \Omega_i^{(j)} \rangle$, tend to reach the value of the frequency of the vibrational mode non-perturbed by the intermolecular resonance, ω_0.

In this case, the role of entropy variations, ΔS_m, as a measure of system disordering becomes dominant in the comparison with the intermolecular interaction energy.

RESULTS AND DISCUSSION

It's known [4] that the temperatures of $CholC_{14}$ phase transitions are 308 K (SC-Sm), 345 K (Sm-Chol) and 351 K (Chol-IL). In the Sm phase the Davydov splitting value decreases sharply and is equal to zero in Chol liquid crystal phase.

The theoretical dependence of the Davydov splitting value on temperature from equation (11) when $p = 2$ has the form:

$$\Delta\Omega_{1,2}^{(j)}(T) = \frac{\Delta\omega_{1,2}^{(j)}}{1 + \exp\left(\frac{\Delta S_1 T - \Delta E_{A1}}{k_B T}\right) + \exp\left(\frac{\Delta S_2 T - \Delta E_{A2}}{k_B T}\right)} \tag{12}$$

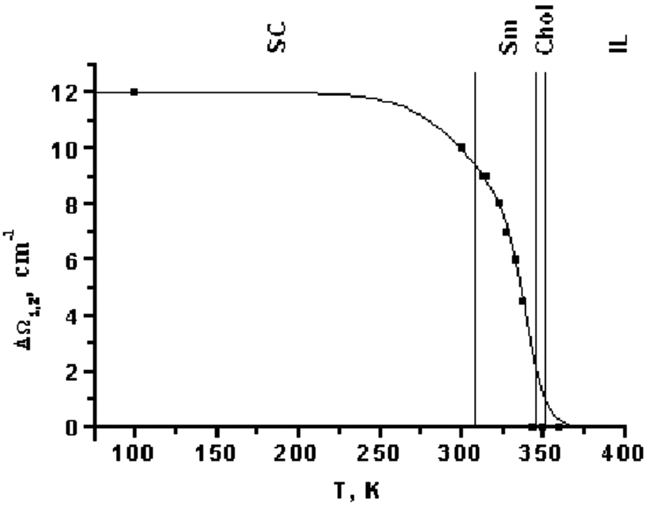

FIGURE 1 Computer fitting for temperature dependence of Davydov splitting value $\Delta\Omega_{1,2}$ for CH_2 in-phase rocking vibrations molecules in cholesteryl myristate ($CholC_{14}$) crystal (dots – experiment, curve – theory).

where $\Delta\omega_{1,2}^{(j)}$ is the value of Davydov splitting of intramolecular vibrations for the crystals in the ordered low-temperature monoclinic phase; ΔS_1, ΔE_1 are, respectively, variations of entropy and activation energy at phase transition SC-Sm; ΔS_2, ΔE_2–corresponding energetic at phase transition Sm-Chol.

The results of our computer fitting of formula (12) (line) to observed (dots) Davydov splitting value temperature dependency presented on Figure 1. Good agreement between the experimental data and the results of such dependence computer fitting is observed. Theoretical estimations of corresponding energetic parameters presented in Table 1.

TABLE 1 The Theoretical Estimations of Energetic Parameters For SC-Sm and Sm-Chol Liquid Crystalline Phase Transitions of Cholesteryl Myristate ($CholC_{14}$) Crystal

ΔE_1, kJ/mole	ΔS_1, kJ/mole·K	ΔE_2, kJ/mole	ΔS_2, kJ/mole·K
27.9 ± 5.1	0.0795 ± 0.017	177.1 ± 4.6	0.523 ± 0.013

CONCLUSIONS

1. In FTIR-spectra for the region of the "order-orientation and position disorder" phase transitions the temperature dependence of Davydov splitting value for the in-phase CH_2 rocking vibrations of crystalline cholesteryl myristate ($CholC_{14}$) has been observed.
2. A statistic and dynamic model is used, which provides an adequate description of this effect. In the frameworks of this model, the damping of vibrational excitons on positional defects of different nature takes place. Genesis of such defects is related with the SC-Sm and Sm-Chol liquid crystal phase transitions.
3. The theoretical analysis of the effects of resonance dynamical intermolecular interactions on the spectra of intramolecular vibrations of the liquid crystals was performed in the terms of stochastic equations, taking into account the SC-Sm and Sm-Chol disordering of the crystalline lattice. Computer fitting of such dependence was performed and theoretical estimations of corresponding energetic parameters of liquid crystal phase transitions were obtained. Good agreement between the experimental and computer fitting results was obtained.

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